

Part I. The Action of Aromatic Grignard
Reagents on Arsenic Trioxide. Part II.
The Action of Aromatic Grignard Re-
agents on Arylarsine Oxides. Part
III. The Preparation and Prop-
erties of Tetra-aryldiarsyls

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
F. D. Smith
1929

EASTON, PA :
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Part I. The Action of Aqueous Glycerol
Reagents on Aqueous Tissues. Part II
The Action of Aqueous Glycerol on
Aqueous Tissues. Part III
The Preparation and Properties
of Tissue Glycerol



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FRANKLIN DANFORD SMITH



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General Introduction¹

A great variety of organic derivatives of tri- and pentavalent arsenic have been prepared. Some of these compounds are not only of interest as chemical individuals but are of great importance as therapeutic agents. In general it seems that inorganic as well as organic derivatives of pentavalent arsenic are much less potent physiologically than those of trivalent arsenic. It would be of considerable interest to know the properties of divalent arsenic compounds and especially important to test them with regard to their value as trypanocides and spirocheticides; we decided, therefore, to attempt the preparation of a series of such compounds.

Since triarylmethyl, R_3C- , and diaryl nitrogen, R_2N- , groups have been shown to exist in the free state as radicals it seemed possible that divalent arsenicals of the type R_2As- might be isolated provided the arsenic atom was attached to suitable aromatic nuclei. It might be expected that such radicals would be formed by spontaneous dissociation of tetraaryldiarsyls, $R_2As-AsR_2$. Tetraphenyldiarsyl has been prepared by the reduction of tetraphenylarsyl oxide, $(C_6H_5)_2As-O-As(C_6H_5)_2$, with phosphorous acid. Several investigators have examined this diarsyl with regard to its tendency to dissociate into diphenylarsyl but the results obtained from molecular weight determinations indicate that the diarsyl undergoes association rather than dissociation. Nevertheless, it seemed to us that tetra-aryldiarsyls might be found which would dissociate into diarylarsyls.

In Part I of this Dissertation we have described improved methods for the preparation of a series of simple aromatic tetraarylarsyl oxides, $RRAs-O-AsRR$. Part II is devoted to methods of preparation of mixed tetraarylarsyl oxides, $RR'As-O-AsR'R$. In Part III we have shown that a number of tetraaryldiarsyls can be prepared readily by the interaction of diarylarsyl iodides and mercury. The diarylarsyl iodides are obtained by a series of simple reactions from the tetraarylarsyl oxides.

The tetra-aryldiarsyls are so extremely reactive, especially toward oxygen, that it seems that their behavior can be accounted for best on the assumption that they exist, to some extent at least, in the form of their dissociation products, the diarylarsyls: $R_2As-AsR_2 \rightleftharpoons 2R_2As-$.

¹ This investigation was made with the assistance of the Parke, Davis and Company Fellowship and we wish to express our appreciation for the aid which has been given us.

PART I

THE ACTION OF AROMATIC GRIGNARD REAGENTS ON ARSENIC TRIOXIDE

This investigation is the first part of a study of certain arsenicals which we synthesized in the hope that they might be found to be of value as spirocheticides.

Tetra-arylsyl oxides,² which were required for the preparation of other compounds, can be obtained quite readily by the interaction of aromatic Grignard reagents and arsenic trioxide; in addition to the oxides there are usually obtained varying amounts of triarylsarsines. Hitherto there has been lack of agreement among various investigators regarding the optimum conditions for the formation of these compounds and the reaction mechanism by which they are produced.

Sachs and Kantorowicz³ state that at a low temperature phenylmagnesium bromide and arsenic trioxide react to form tetraphenylarsyl oxide, while at a higher temperature triphenylarsine is produced. They claim, furthermore, that *p*-tolylmagnesium bromide and arsenic trioxide yield only tri-*p*-tolylarsine, regardless whether the reaction is carried out at a low or high temperature.

Recently, Matsumiya and Nakai⁴ found that phenylmagnesium bromide and arsenic trioxide yield invariably a mixture of tetraphenylarsyl oxide and triphenylarsine, both at low and high temperatures; similar results were obtained with *p*-tolylmagnesium bromide, but in the case of α -naphthylmagnesium bromide only one product seemed to be formed, a compound stated to be either $(C_{10}H_7)_4As_2O \cdot H_2O$ or $(C_{10}H_7)_2As(OH)$. Experimental evidence which we obtained indicates that neither of these formulas is correct. If the compound possessed the first of the above formulas it should react with ethylmagnesium bromide with the liberation of two molecular equivalents of ethane; a compound of the second type should yield one equivalent of the gas. It was found that no gas was evolved when the naphthyl compound was treated with ethylmagnesium bromide. Furthermore, we found the molecular weight of the substance to be 680. The

² It seems to us that the use of the term "arsyl" [Steinkopf and Smie, *Ber.*, **59**, 1456 (1926)] permits one to apply a more rational system of nomenclature to the arsenic compounds which we have investigated than that commonly used. We have called AsH_3 and AsR_3 , arsine and triarylsarsine, respectively; $-AsH_2$ and $-AsR_2$, arsyl and diarylsarsyl; $H_2As-O-AsH_2$ and $R_2As-O-AsR_2$, arsyl oxide and tetra-arylsarsyl oxide; $H_2As-AsH_2$, diarsyl and $R_2As-AsR_2$, tetra-aryldiarsyl.

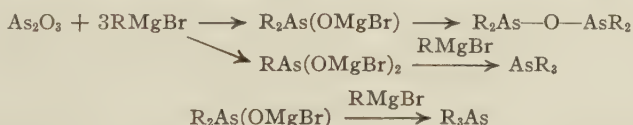
³ Sachs and Kantorowicz, *Ber.*, **41**, 2767 (1908).

⁴ Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 307 (1925).

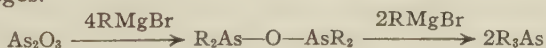
naphthyl compound, therefore, seems to possess the normal structure $(C_{10}H_7)_2As-O-As(C_{10}H_7)_2$.

We have studied the action of arsenic trioxide on phenyl-, *p*-tolyl-, *p*-anisyl-, α -naphthyl- and biphenylmagnesium halides. In the case of some of the tetra-arylsarsyl oxides we have greatly increased the yields obtained by other investigators by the use of procedures which are fully described in the experimental part of this paper. Tetrabiphenylarsyl oxide has not been prepared hitherto. With the first three Grignard reagents mentioned above, mixtures of tetra-arylsarsyl oxides and triarylsarsines were obtained, regardless of the way in which the experimental conditions were varied, but with the last two arylmagnesium halides only tetra-arylsarsyl oxides were found to be formed.

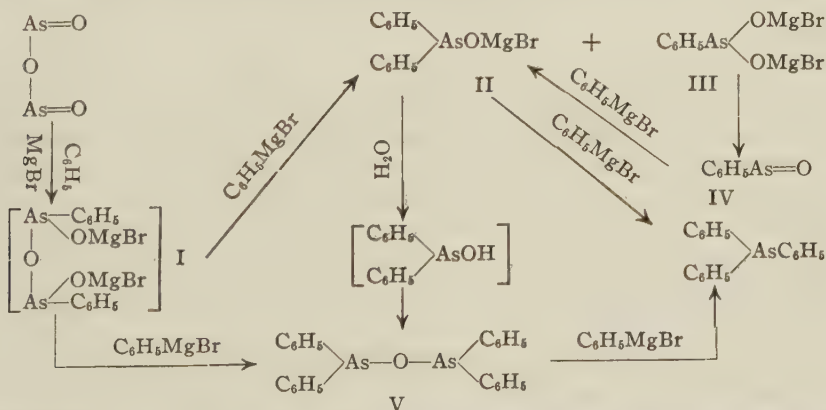
Concerning the manner in which the tetra-arylsarsyl oxides and the triarylsarsines are produced, Sachs and Kantorowicz suggested the following scheme but gave no experimental evidence in support of their view.



Matsumiya and Nakai, as well as Gryszkiewicz-Trochimowski and Zambrzycki,⁵ who studied the action of phenylmagnesium bromide on arsenic trioxide, considered it probable that the reaction proceeded in the following stages.



A consideration of the various possible reactions which might take place when a Grignard reagent, phenylmagnesium bromide for example, reacts with arsenic trioxide leads to the following formulation.



⁵ Gryszkiewicz-Trochimowski and Zambrzycki, *Roczniki Chemii*, **6**, 798 (1926).

One of the first questions which arises in connection with the study of the mechanism of the reaction is this: Is tetraphenylarsyl oxide, V, formed directly from the inorganic oxide (possibly through intermediate formation of I) or is it produced from Compound II by the addition of water to the reaction mixture?

When phenylmagnesium bromide reacts with arsenic trioxide, in the presence of a mixture of ether and benzene, a heavy precipitate soon forms. After completion of the reaction and the removal of most of the ether, the precipitate was separated from the solvent and decomposed with water. Four-fifths of the total amount of tetraphenylarsyl oxide formed was obtained from the precipitate, while the remainder of the arsyl oxide and triphenylarsine was isolated from the benzene layer. If tetraphenylarsyl oxide had been formed directly from arsenic trioxide, and hence were present as such in the reaction mixture, it seems that *all* of the tetraphenylarsyl oxide should have been obtained from the benzene layer and none from the precipitate;⁶ more than enough solvent was employed to hold in solution all of the tetraphenylarsyl oxide which could possibly have been formed from the amount of arsenic trioxide used.

It seems to us that the above phenomena may be accounted for if the assumption is made that $(C_6H_5)_2As-OMgBr$, a substance which might be expected to be only slightly soluble in benzene, is the precursor of tetraphenylarsyl oxide and that the latter compound is produced only after the addition of water to the precipitate mentioned above.

The same type of phenomenon was encountered in the case of α -naphthyl- and biphenylmagnesium bromide except that in the latter instance all of the tetra-aryl oxide was obtained from the precipitate after decomposition of the latter with water. No precipitates, however, were formed with the tolyl- and anisylmagnesium halides. We can only suggest that in these instances the compounds of the type $R_2As-OMgX$ may be more soluble.

Compound IV, which would probably be produced by spontaneous decomposition of III, could not be found among the reaction products from phenylmagnesium bromide and arsenic trioxide. We have shown that this substance reacts with phenylmagnesium bromide to form either a mixture of tetraphenylarsyl oxide and triphenylarsine or is converted quantitatively into triphenylarsine, depending on experimental conditions. It was found, also, that tetraphenylarsyl oxide, under proper conditions, reacts with phenylmagnesium bromide to form triphenylarsine in quantitative yield.

Finally, we prepared a number of diarylarsyl halides, some of which have not been described previously.

⁶ This consisted, in part, of inorganic magnesium salts.

Experimental Part

Aromatic Grignard Reagents and Arsenic Trioxide^{7,8} Phenylmagnesium Bromide.—

The reagent was prepared from 62.8 g. of bromobenzene (0.4 mole), 9.7 g. of magnesium (0.4 mole) and 200 cc. of ether in a liter, three-necked flask, fitted with a reflux condenser and then diluted with an equal volume of benzene. The flask was cooled in an ice-bath and a mechanical stirrer introduced. In this experiment, as well as in all of the following ones, moisture was prevented from entering the apparatus. Nineteen and eight-tenths g. (0.1 mole) of dry arsenic trioxide was added as rapidly as possible while the mixture was stirred vigorously. It was found that rapid addition of the arsenic trioxide to the thoroughly cooled reaction mixture reduced the amount of triphenylarsine to a minimum. After all of the oxide had been added, the ice-bath was removed. A colorless precipitate, probably $(C_6H_5)_2AsOMgBr$ and inorganic magnesium salts, soon formed with the evolution of considerable heat.

After the mixture had been stirred for four hours, the solvent was removed under diminished pressure, in a stream of dry nitrogen, until the reaction mixture was reduced to about one-third of its original volume. When the solid material had settled, the benzene layer was decanted and the former substance was decomposed with ice and a small amount of acetic acid. The organic material was extracted with benzene, the benzene solution was shaken with dilute aqueous sodium hydroxide and then dried with fused sodium sulfate. The solvent was removed on a steam-bath and the oily residue allowed to solidify. The material was washed thoroughly with petroleum ether (40–60°) and then with a mixture of ether and petroleum ether; m. p. 92.5–93.5°. This substance was pure tetraphenylarsyl oxide. The yield was 21 g.

The solvents with which the tetraphenylarsyl oxide had been washed were now added to the benzene layer mentioned above and the mixture was treated with ice and a small amount of acetic acid. After separation of the benzene layer, the latter was washed with dilute sodium hydroxide solution, dried and the solvent removed. The oily residue solidified to an amorphous mass. After the latter had been treated with petroleum ether several times, it melted at 91–92° and hence was tetraphenylarsyl oxide; yield, 5 g. The total yield of this oxide was 26 g., or 55% of the calculated amount. The petroleum ether with which the above material had been washed was concentrated to a very small volume and then diluted with 25 cc. of dry ether. Upon the addition of mercuric chloride dissolved in ether the mercuric chloride addition product of triphenylarsine was precipitated. The latter weighed 10.2 g. and corresponds to 5.4 g. of triphenylarsine.

The following experiment shows that triphenylarsine is precipitated practically quantitatively by mercuric chloride: 6.12 g. of pure triphenylarsine was dissolved in a small amount of absolute ether. Upon the addition of 5.42 g. of dry mercuric chloride, dissolved in 250 cc. of ether, a precipitate was obtained which weighed 11.30 g.; calcd. weight of addition product, 11.54 g. Triphenylarsine can be obtained from the addition product if the latter is suspended in alcohol and then treated with hydrogen sulfide.

⁷ Very little information is to be found in the literature regarding the action of aliphatic Grignard reagents on arsenic trioxide. Sachs and Kantorowicz, *Ber.*, **41**, 2769 (1908), state that *iso*-amylmagnesium bromide reacts with arsenic trioxide with the formation of an oil. Gryszkiewicz-Trochimowski and Zambrzycki, *Roczniki Chemij*, **6**, 749 (1926), studied the action of methyl-, ethyl-, propyl- and allylmagnesium halides on arsenic trioxide and were able to isolate only trialkylarsines in rather poor yields.

⁸ Recently, Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **10**, 57 (1927), published their results on the action of arylmagnesium halides on arsenic trisulfide. They obtained triarylsines and varying amounts of tetra-arylsyl sulfides.

In one experiment an attempt was made to account for all of the material used. From 19.8 g. of arsenic trioxide and 62.8 g. of bromobenzene there were obtained 29 g. of tetraphenylarsyl oxide (equivalent to 12.1 g. of arsenic trioxide and 38.4 g. of bromobenzene), 10.2 g. of the mercuric chloride addition product of triphenylarsine (equivalent to 1.7 g. of arsenic trioxide and 8.3 g. of bromobenzene), 3.5 g. of biphenyl (equivalent to 7.1 g. of bromobenzene), 5.4 g. of unchanged arsenic trioxide and a small amount of phenol. The total amount of bromobenzene thus accounted for is 53.8 g., or 85.5% of that used; the amount of arsenic trioxide, 19.3 g., or 97% of that employed.

After conversion of the oxide into diphenylarsyl chloride, purification of the latter by distillation and hydrolysis of the chloride into the original oxide, the latter was recrystallized from alcohol; m. p. 95.5–96.5°. The highest melting point recorded previously was 92.5–93.5°.⁹

***p*-Tolylmagnesium Bromide.**—After 68.4 g. of *p*-bromotoluene and 9.7 g. of magnesium in 200 cc. of ether had reacted completely, the solution was diluted with 200 cc. of dry benzene. The contents of the flask were then cooled, stirred vigorously and 19.8 g. of dry arsenic trioxide was added as quickly as possible. In this instance no precipitate formed. The mixture was stirred for four hours and then decomposed with ice and a small amount of acetic acid. The ether–benzene layer was separated, washed with dilute sodium hydroxide solution and then dried with fused sodium sulfate. The solvent was removed and the oily residue dissolved in absolute ether. The ether solution was treated with mercuric chloride dissolved in ether until a precipitate no longer formed. The precipitate, which was the mercuric chloride addition product of tritolylarsine, was removed by filtration. The filtrate was shaken with dilute hydrochloric acid to remove mercuric chloride, dried and the solvent removed. The solid residue was washed thoroughly with petroleum ether (40–60°). The yield of tetra-*p*-tolylarsyl oxide was 25.5 g., or 48% of the calculated amount. After recrystallization from alcohol the compound melted at 108.5–109.5°. The amount of tritolylarsine formed, calculated on the basis of the addition product, was 9 g.

Sachs and Kantorowicz³ obtained only tritolylarsine but no arsyl oxide from *p*-tolylmagnesium bromide and arsenic trioxide. From the interaction of the two latter substances Matsumiya and Nakai¹⁰ obtained a 10% yield of tetratolylarsyl oxide and recorded the melting point as 105–106°.

***p*-Anisylmagnesium Iodide.**—The Grignard reagent was prepared from 93.6 g. of *p*-iodo-anisole,¹¹ 9.7 g. of magnesium and 250 cc. of ether. Two hundred and fifty cc. of dry benzene was then added; the subsequent procedure was the same as that described above for *p*-tolylmagnesium bromide.

There was obtained 33 g. of tetra-*p*-anisylarsyl oxide; m. p. 127–129°. This corresponds to a yield of 56%. In addition, 12 g. of trianisylarsine was formed.

Tetra-*p*-anisylarsyl oxide had been obtained previously by Michaelis and Weitz,¹² by the action of hydriodic acid on tri-*p*-anisylarsine and subsequent hydrolysis of the dianisylarsyl iodide. The substance obtained by them melted at 130°.

α -Naphthylmagnesium Bromide.—This reagent was prepared from 91 g. of pure α -bromonaphthalene¹³ (0.44 mole), 9.7 g. of magnesium (0.40 mole) and 200 cc. of ether. An equal volume of benzene was then added to prevent the separation of solid naphthylmagnesium bromide from the solution. The mixture was stirred vigorously and 19.8 g. (0.10 mole) of arsenic trioxide was added. During the latter operation no external

⁹ McKenzie and Wood, *J. Chem. Soc.*, **117**, 412 (1920).

¹⁰ Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 312 (1925).

¹¹ Blicke and Smith, *J. Am. Chem. Soc.*, **50**, 1229 (1928).

¹² Michaelis and Weitz, *Ber.*, **20**, 50 (1887).

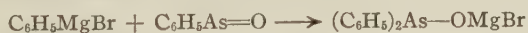
¹³ Blicke, *J. Am. Chem. Soc.*, **49**, 2846 (1927).

cooling was necessary. After some time a heavy precipitate formed. The mixture was stirred for four hours and then ice and a small quantity of acetic acid were added. The mixture was shaken vigorously and after a short time two distinct layers formed rather suddenly. The ether-benzene layer was then decanted immediately. Within a few minutes tetra- α -naphthylarsyl oxide began to separate, and was completely precipitated after a few hours. The organic oxide was filtered and air-dried. The material was recrystallized from tetralin, suspended in hot benzene to remove any tetralin and filtered; m. p. 250–253° with decomposition. The yields of crude tetranaphthylarsyl oxide averaged 52 g., which corresponds to 77% of the calculated amount. No trinaphthylarsine could be discovered among the reaction products. From α -bromonaphthalene and arsenic trioxide Matsumiya and Nakai¹⁴ obtained a 32% yield of the arsyl oxide. They found the melting point of the substance to be 240–241°.

***p*-Bromobiphenylmagnesium Bromide.**—The Grignard compound was prepared from 31 g. of *p*-bromobiphenyl,¹⁵ 4.0 g. of magnesium and 200 cc. of ether in a 500-cc. round-bottomed flask which had been modified in the following manner. A glass tube 1 cm. wide and about 15 cm. long was sealed to the body of the flask a short distance from the neck of the latter. About 3 cm. beyond the point of attachment the glass side arm was bent at a right angle toward the bulb of the flask. During the preparation of the Grignard reagent the arm of the flask was closed with a cork. After the above mixture had been heated for about ten hours, the solution of the Grignard reagent was decanted through the side arm from unchanged magnesium and dibiphenyl into a liter 3-necked flask which had been fitted with a reflux condenser and a mechanical stirrer. Two hundred cc. of dry benzene and 100 cc. of ether were added to the mixture and the latter was cooled and stirred vigorously. Upon addition of the arsenic trioxide (6.6 g.) a vigorous reaction took place. A precipitate soon formed which coated the surface of the unchanged inorganic oxide. The reaction mixture was stirred for four hours and the precipitate was then allowed to settle. After twelve hours the liquid layer was decanted¹⁶ and the solid material decomposed as usual. The organic matter was extracted with benzene; the benzene solution was dried and filtered. After removal of the solvent 10 g. of crude tetra-*p*-biphenylarsyl oxide was obtained; this yield corresponds to 39% of the calculated amount. The crude material melted about 132–138°. After conversion of the oxide into the chloride, recrystallization of the latter and hydrolysis into the tetra-arylarsyl oxide, the substance melted at 150–152°.

From the experiments described below it can be seen that in the interaction of phenylmagnesium bromide with phenylarsyl oxide, $(C_6H_5)_3As=O$ (or with $(C_6H_5)_2As-OMgBr$), a large excess of the arylmagnesium halide favors the formation of triphenylarsine to a very decided extent. In the first instance there was used twice the amount of phenylmagnesium bromide necessary for the formation of the arsine; in the second instance eight times the calculated amount of Grignard reagent.

Phenylmagnesium Bromide and Phenylarsine Oxide.—Presumably these two compounds react first in accordance with the following



The diaryl compound then reacts with the Grignard reagent to form the tertiary arsine.

¹⁴ Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 313 (1925).

¹⁵ Gomberg and Bachmann, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 42.

¹⁶ Upon evaporation of the solvent only biphenyl was obtained.

1. Phenylmagnesium bromide was formed from 5.7 g. of bromobenzene (0.037 mole), 0.9 g. of magnesium and 25 cc. of ether. After the addition of 2.7 g. of phenylarsine oxide (0.016 mole), dissolved in 25 cc. of benzene, the mixture was refluxed for three hours. There was obtained 3.0 g. of tetraphenylarsyl oxide and 0.5 g. of triphenylarsine.

2. The Grignard reagent was prepared from 31.4 g. of bromobenzene (0.2 mole), 4.8 g. of magnesium and 100 cc. of ether. Four and two-tenths g. of phenylarsine oxide (0.025 mole), dissolved in 100 cc. of benzene, was added and the mixture was refluxed for four hours. No tetraphenylarsyl oxide was formed. The yield of triphenylarsine was 7.4 g., or 97% of the calculated amount.

The following experiments show that triphenylarsine is produced by interaction of phenylmagnesium bromide with tetraphenylarsyl oxide. Inasmuch as the Grignard reagent and the arsyl oxide react readily even at 0° to form the arsine, it seems impossible to prevent the formation of the latter substance in the preparation of the tetra-arylsyl oxide.

Phenylmagnesium Bromide and Tetraphenylarsyl Oxide.—The Grignard reagent was prepared from 7.3 g. of bromobenzene (0.05 mole), 0.8 g. of magnesium and 30 cc. of ether. The solution was cooled to 0° and 4.7 g. of tetraphenylarsyl oxide (0.01 mole) was added. After the mixture had remained at 0° for four hours, a heavy crystalline precipitate had formed. The ether layer was decanted from the crystalline deposit and decomposed with ice and ammonium chloride. The ether solution was dried with fused sodium sulfate and the triphenylarsine was precipitated by means of mercuric chloride. The mercuric chloride addition product was removed by filtration and the filtrate was shaken with dilute hydrochloric acid to remove excess mercuric chloride. The ether solution was dried again and the solvent removed. The pasty residue was washed with low-boiling petroleum ether to remove biphenyl. The product which remained was tetraphenylarsyl oxide. The crystalline deposit was decomposed with ice and ammonium chloride and after the addition of a small amount of ether to dissolve the material the solution was treated as described above. Tetraphenylarsyl oxide and triphenylarsine were obtained. The total yield of oxide was 2.6 g.; that of arsine was 2.1 g.

In a second experiment the reaction mixture was kept somewhat above 35°. Phenylmagnesium bromide was prepared from 31.4 g. of bromobenzene (0.2 mole), 4.8 g. of magnesium and 100 cc. of ether. Eleven and eight-tenths g. of tetraphenylarsyl oxide (0.04 mole), dissolved in 100 cc. of benzene, was added and the mixture was refluxed for four hours. The yield of triphenylarsine was 14.2 g.; the calculated amount is 15.3 g.

Finally, we found that arsenic trioxide and an excess of phenylmagnesium bromide react quantitatively to form triphenylarsine. Five g. of arsenic trioxide (0.025 mole) and the Grignard reagent (0.4 mole) obtained from 62.8 g. of bromobenzene, 9.7 g. of magnesium and 200 cc. of ether were refluxed for four hours. There was obtained 15.0 g. of triphenylarsine; the calculated amount of triphenylarsine is 15.2 g.

TABLE I
DIARYLSYLSYL HALIDES

	M. p., °C.	Formula	Analysis (Volhard)	
			Calcd.	Found
1 Diphenylarsyl chloride	40–42 ^a			
2 Diphenylarsyl bromide	52–54 ^b			
3 Diphenylarsyl iodide	42–43 ^c			
4 Di- <i>p</i> -tolylarsyl chloride	44–45 ^d			
5 Di- <i>p</i> -tolylarsyl bromide	65–66	C ₁₄ H ₁₄ AsBr	Br, 23.73	23.65, 23.70

TABLE I (Concluded)

	M. p., °C.	Formula	Analysis (Volhard)	
			Calcd.	Found
6 Di- <i>p</i> -tolylarsyl iodide	64-65	C ₁₄ H ₁₄ AsI	I, 33.07	33.10, 33.02
7 Di- <i>p</i> -anisylarsyl chloride	83-84 ^a			
8 Di- <i>p</i> -anisylarsyl bromide	60-62	C ₁₄ H ₁₄ O ₂ AsBr	Br, 21.68	21.20, 21.22
9 Di- <i>p</i> -anisylarsyl iodide	40-42 ^f	C ₁₄ H ₁₄ O ₂ AsI	I, 30.52	30.60, 30.43
10 Di- <i>p</i> -naphthylarsyl chloride	167-168 ^g			
11 Di- <i>p</i> -naphthylarsyl bromide	172-173	C ₂₀ H ₁₄ AsBr	Br, 19.56	19.45, 19.41
12 Di- <i>p</i> -naphthylarsyl iodide	140-141	C ₂₀ H ₁₄ AsI	I, 27.85	27.65, 27.70
13 Dibiphenylarsyl chloride	145-147	C ₂₄ H ₁₈ AsCl	Cl, 8.52	8.48, 8.45
14 Dibiphenylarsyl bromide	147-149	C ₂₄ H ₁₈ AsBr	Br, 17.35	17.54, 17.23
15 Dibiphenylarsyl iodide	140-141	C ₂₄ H ₁₈ AsI	I, 25.00	24.73, 24.80

The chlorides were prepared from the tetra-arylsarsyl oxides and hydrogen chloride; the bromides from the oxides and hot 48% hydrobromic acid; the iodides from the chlorides and sodium iodide in acetone.

Compounds 1, 2, 3, 4, 5, 6, 7, 8 and 9 were recrystallized from absolute alcohol; 10, 11, 12, 13 and 15 from benzene; 14 from a mixture of benzene and absolute alcohol.

^a The m. p. recorded by Norris, *J. Ind. Eng. Chem.*, **11**, 824 (1919), is 34°.

^b Michaelis and La Costa, *Ann.*, **201**, 230 (1880), described the compound as an oil; Pope and Turner, *J. Chem. Soc.*, **117**, 1452 (1920), give the m. p. as 55-56°; Steinkopf and Schwen, *Ber.*, **54**, 1459 (1921), record the m. p. as 54°.

^c The m. p. given by Pope and Turner^b is 45-46°; Steinkopf and Schwen^b state the m. p. to be 40.5°.

^d La Costa, *Ann.*, **208**, 18 (1881), recorded the m. p. as 31°; Michaelis, *Ann.*, **321**, 160 (1902), as 45°.

^e Michaelis and Weitz, *Ber.*, **20**, 50 (1887), found the m. p. to be 79-80°.

^f Michaelis and Weitz^e obtained the substance as an oil.

^g Matsumiya, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **4**, 217 (1920).

Summary

A reaction mechanism has been suggested to account for the products which are formed from the interaction of aromatic Grignard reagents and arsenic trioxide.

Improved methods have been described for the preparation of tetraphenyl-, tetra-*p*-tolyl-, tetra-*p*-anisyl- and tetra- α -naphthylarsyl oxides. Tetra-*p*-biphenylarsyl oxide has been synthesized.

A number of diarylhalo-arsines have been prepared and described.

PART II

THE ACTION OF AROMATIC GRIGNARD REAGENTS ON ARYLARSINE OXIDES

A second method for the preparation of tetra-arylarstyl oxides, by means of which simple as well as mixed oxides of the type $RR'As-O-AsR'R$ can be obtained, is the subject of this paper.

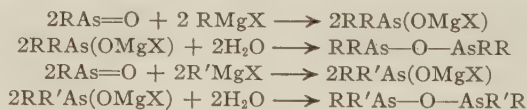
Diphenyl, di-*p*-tolyl, di-*p*-anisyl and di- α -naphthyl mercury were prepared by the interaction of arylmagnesium halides and mercuric chloride. $RMgX + HgCl_2 \longrightarrow RHgX + ClMgX$; $RHgX + RMgX \longrightarrow RHgR + MgX_2$. Hitherto only diphenylmercury has been obtained by this method.¹

The diarylmercury compounds were heated with arsenic trichloride with the formation of aryldichloro-arsines which, upon hydrolysis, yielded arylarsine oxides.



In those instances in which it is impractical to prepare the mercury diaryls, the oxides can be obtained by reduction of the corresponding diarylarsonic acids.

The arylarsine oxides, when allowed to react with an aromatic Grignard reagent, were converted into tetra-arylarstyl oxides, as follows

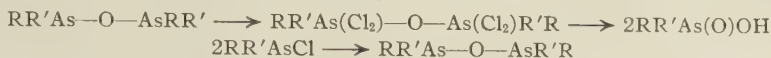


The simple tetra-arylarstyl oxides were obtained directly from the reaction mixture in crystalline form. The mixed oxides, however, could be isolated only in the form of oils which would not crystallize. These products were treated with chlorine,² the crystalline tetrachlorides hydrolyzed to the arsonic acids, the latter reduced and the reduction products

¹ Pfeiffer and Truskier, *Ber.*, **37**, 1127 (1904).

² In some instances the tetra-arylarstyl oxides were oxidized directly to the diarylarsonic acids by means of warm alkaline hydrogen peroxide.

isolated in the form of the diarylarsyl halides. The latter when hydrolyzed yielded the pure tetra-arylarsyl oxides



Experimental Part

Preparation of Mercury Diaryls

General Procedure.—The Grignard reagent was prepared in a liter, three-necked flask from 0.4 mole of the aryl halide, 0.4 of an atomic equivalent of magnesium and 200 cc. of ether. A mechanical stirrer was introduced and the arylmagnesium halide diluted with 100 cc. of dry benzene. Forty-eight g. (0.18 mole) of dry mercuric chloride was added, cautiously, in four portions during the course of an hour with rapid stirring; the stirring was continued for eight hours. The reaction mixture, which consisted of the mercury diaryl and the arylmercuric halide, was treated with ice and a small amount of hydrochloric acid. In the case of mercury diphenyl, the ether-benzene layer was decanted, filtered and dried with fused sodium sulfate. The solvent was removed and the residue washed with petroleum ether (40–60°). In the preparation of mercury ditolyl only a small amount of the substance is present in the ether-benzene layer and in the case of mercury dianisyl and mercury dinaphthyl practically all of the material is found in the reaction mixture as a precipitate. In the latter instance the dry mixture of the mercury diaryl and the arylmercuric halide was placed in a Soxhlet apparatus and the diaryl mercury extracted with benzene.

TABLE I
MERCURY DIARYLS

	Diphenyl ^a	Di- <i>p</i> -tolyl ^b	Di- <i>p</i> -anisyl ^b	Di- α -naphthyl ^c
M. p., °C.	121	235–238	198–200	240–243
Yield, %	75	70	62	90

^a Pfeiffer and Truskier, ref. 4, obtained a 42% yield; m. p. 120°. ^b Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921. ^c Matsumiya, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **8**, 394 (1925), obtained this compound from α -naphthylmagnesium bromide and α -naphthyl mercuric chloride in 69% yield.

Preparation of Arylarsine Oxides

General Procedures (a).—The mercury diaryl was heated with one and one-half times the theoretical amount of freshly distilled arsenic trichloride for three hours at 130–140°. The reaction mixture was extracted with benzene and filtered. After removal of most of the benzene on a steam-bath, the mixture was distilled under diminished pressure in an atmosphere of nitrogen until the excess arsenic trichloride had been removed. The crude aryldichloro-arsine was added to a warm 10% solution of sodium hydroxide with rapid stirring; sufficient alkali should be used to dissolve all of the arylarsine oxide formed. The solution was filtered from mercury compounds through a Jena filter. The alkaline filtrate was neutralized, the precipitate washed by decantation and then filtered.

The oxides, with the exception of the naphthyl compound, were dissolved in hot benzene and an equal volume of absolute ether added to the cold benzene solution. The oxides precipitated slowly. The naphthylarsine oxide was obtained in a pure state in the following manner: the crude oxide was suspended in benzene, treated with dry hydrogen chloride and the solution of naphthylidichloro-arsine heated until the solvent was removed. A small amount of petroleum ether (40–60°) was added to the oily residue. The latter became crystalline and the material was then recrystallized from

petroleum ether; m. p. 70–72°. Upon hydrolysis of the dichloride there was obtained pure naphthylarsine oxide.

(b) Sulfur dioxide was passed into a mixture prepared from one part of the arylarsonic acid,⁴ five parts of methyl alcohol, two parts of concd. hydrochloric acid and about 0.1 g. of potassium iodide dissolved in a small amount of water. The greater part of the aryl-dichloro-arsine formed precipitated as an oil. Water was added to precipitate the chloride completely and after decantation of the aqueous layer the oil was washed thoroughly with water. The oily chloride was treated with warm 10% sodium hydroxide until a clear solution was obtained. The latter was neutralized, whereupon the arylarsine oxide precipitated.

TABLE II
ARYLARSINE OXIDES

	Phenyl	<i>p</i> -Tolyl	<i>p</i> -Anisyl	α -Naphthyl
M. p., °C.	144–146 ^a	188–190 ^b	114–116 ^c	245 ^d
Yield (method a), ^e %	60			60
Yield (method b), ^f %	80	87	90	..

^a Michaelis, *Ber.*, 10, 623 (1877), recorded the melting point as 119–120°. Gryszkiewicz-Trochimowski, Mateyak and Zablotski, *Bull. soc. chim.*, [4] 41, 1327 (1927), state that the substance melts at 129–130° when prepared by hydrolysis of phenyl-dicyano-arsine. ^b La Coste and Michaelis, *Ann.*, 201, 257 (1880), found the melting point to be 156°. Tolyldichloro-arsine, from which this oxide was prepared by hydrolysis, was analyzed. Calcd. for C₇H₇AsCl₂: Cl, 29.95. Found: 29.87, 29.65. ^c Michaelis and Weitz, *Ber.*, 20, 51 (1887), described this substance as a crystalline crust but recorded no melting point. When this compound is recrystallized from a mixture of benzene and ether, it melts at 93–95° and seems to lose solvent of crystallization. After it has been heated it melts at 114–116°. The latter melting point was obtained when the compound was recrystallized from a mixture of chloroform and ether. ^d If the oxide is dissolved in alkali, precipitated with an acid and then air dried it melts at 245°. After recrystallization from tetralin the melting point was 206–210°. When the compound obtained from tetralin was heated with benzene the melting point was 185–190°. Solvent of crystallization can be seen to escape from the melting-point tube when the latter is heated. ^e The yield is based on the diaryl mercury compound. ^f The yield is based on the arylarsinic acid which had been recrystallized from water.

Interaction of Arylmagnesium Halides and Arylarsine Oxides

General Procedure.—Three hundredths of a mole of the arylarsine oxide was dissolved in 100 cc. of dry benzene, the solution cooled with ice and stirred rapidly. Forty-five hundredths of a mole of the Grignard reagent was then added. After one-half hour the ice-bath was removed and the mixture was stirred for four hours longer. After twelve hours the reaction mixture was decomposed with ice and a small amount of acetic acid, the ether–benzene layer separated, washed with 10% sodium hydroxide and then dried over fused sodium sulfate. The solvents were removed and the oily residue, which could not be obtained in crystalline form in the case of the mixed tetra-arylsyl oxides, RR'As—O—AsR'R, was dissolved in absolute ether and the solution saturated with chlorine. The tetrachloro derivative of the tetra-arylsyl oxide precipitated to some extent in the form of an oil which soon became crystalline. The solvent was removed from the mixture and the residue treated with 5% sodium hydroxide

³ Gryszkiewicz-Trochimowski, Mateyak and Zablotski, *Bull. soc. chim.*, [4] 41, 1328 (1927), record the melting point as 69.5–70°.

⁴ The arylarsonic acids were all prepared according to the method of Schmidt, *Ann.*, 421, 169 (1920).

solution to convert the tetrachloride into the arsenic acid. The alkaline solution of the latter substance was extracted with ether to remove by-products, the solution heated on a steam-bath to remove dissolved ether and then neutralized, whereupon the arsenic acid precipitated in the form of a gum; after some time the latter became solid. The crude arsenic acid was boiled with acetone, the solution cooled and then filtered. This process was repeated several times. The arsenic acid dissolves in the acetone only to a slight extent but the by-products in the crude acid are much more soluble. Phenyl-biphenylarsinic acid can be recrystallized from alcohol.

The diarylarsinic acid was then converted into the diarylarsyl chloride by the action of sulfur dioxide and hydrochloric acid in the same manner as described above under general procedure (b). The diarylarsyl chloride precipitated immediately in some cases as an oil, in other instances as a solid. The chloride was then heated with alcoholic sodium hydroxide, whereby it was converted into the tetra-arylsyl oxide.

TABLE III
DIARYLARSINIC ACIDS^a

	M. p., °C.	Formula	Arsenic analyses ^c	
			Calcd.	Found
Phenyl- <i>p</i> -tolyl	148-150 ^b	C ₁₃ H ₁₃ AsO ₂	27.17	27.65
Phenyl- <i>p</i> -anisyl	167-169	C ₁₃ H ₁₃ AsO ₃	25.68	26.08
Phenyl- α -naphthyl	175-176	C ₁₆ H ₁₃ AsO ₂	24.03	24.87
Phenylbiphenyl	218-220	C ₁₈ H ₁₅ AsO ₂	22.20	22.10
<i>p</i> -Anisylbiphenyl	228-231	C ₁₉ H ₁₇ AsO ₃	20.38	20.59

^a All of the diarylarsinic acids are practically insoluble in hot acetone, soluble in a mixture of alcohol and hydrochloric acid, soluble in hot benzene and only slightly soluble in hot water. ^b Michaelis, *Ann.*, **321**, 157 (1902), recorded the melting point as 158-160°. ^c Ewin, *J. Chem. Soc.*, **109**, 1356 (1916).

TABLE IV
DIARYLARSYL CHLORIDES

	M. p., °C.	Formula	Chlorine analyses (Volhard)	
			Calcd.	Found
Phenyl- <i>p</i> -tolyl ^a	Oil	C ₁₃ H ₁₂ AsCl	12.73	12.67
Phenyl- <i>p</i> -anisyl	Oil	C ₁₃ H ₁₂ OAsCl	12.04	12.26
Phenyl- α -naphthyl	Oil	C ₁₆ H ₁₂ AsCl	11.27	11.12
Phenylbiphenyl	83-85°	C ₁₈ H ₁₄ AsCl	10.41	10.31
<i>p</i> -Anisylbiphenyl	Oil	C ₁₉ H ₁₆ OAsCl	9.57	10.01

^a Michaelis, Table III, footnote *b*, states that this substance is an oil.

TABLE V
TETRA-ARYLARSYL OXIDES^a

	Reagents for the preparation		M. p., °C.
	Oxide	Mg compound	
Diphenyl-di- <i>p</i> -tolyl ^a	Phenylarsine	Phenyl-Mg-bromide	75-77
Diphenyl-di- <i>p</i> -anisyl	Phenylarsine	Anisyl-Mg-iodide	Oil
Diphenyl-di- α -naphthyl	Phenylarsine	Naphthyl-Mg-bromide	Oil
Diphenyldibiphenyl	Phenylarsine	Biphenyl-Mg-bromide	124-126
Di- <i>p</i> -anisylbiphenyl	Anisylarsine	Biphenyl-Mg-bromide	Oil
Tetra- <i>p</i> -tolyl	Tolylarsine	Tolyl-Mg-bromide	108
Tetra- <i>p</i> -anisyl	Anisylarsine	Anisyl-Mg-iodide	128-129
Tetra- α -naphthyl	Naphthylarsine	Naphthyl-Mg-bromide	250-251

^a Michaelis, footnote *a*, Table II, prepared the substance by the hydrolysis of the chloride, which had been obtained by heating phenyldichloro-arsine with an excess of ditolyl-mercury. He described it as being an oil.

Summary

1. The preparation of diphenyl, di-*p*-tolyl, di-*p*-anisyl and di- α -naphthyl mercury from the interaction of an arylmagnesium halide and mercuric chloride has been described.

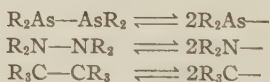
2. Phenyl-, *p*-tolyl-, *p*-anisyl- and α -naphthylarsine oxide have been prepared. Two methods of preparation were used: (a) the diaryl mercury compound was heated with arsenic trichloride and the aryldichloroarsine formed was hydrolyzed; (b) the arylarsonic acid was reduced with sulfur dioxide in the presence of hydrochloric acid and the aryldichloroarsine was hydrolyzed.

3. A number of tetra-arylsarsyl oxides of the type $RR'As-O-AsR'R$ were prepared from the interaction of an arylarsine oxide and an arylmagnesium halide. In addition several mixed diarylsarsinic acids and mixed diarylsarsyl chlorides have been described.

PART III

TETRA-ARYLDIARSYLS

In view of the fact that tetra-arylhydrazines¹ and hexa-arylethanes² dissociate spontaneously into diarylnitrogen radicals and triarylmethyls, respectively, it seemed possible that tetra-aryldiarsyls might behave in a similar manner



Several investigators have studied tetraphenyldiarsyl with regard to its tendency to dissociate into diphenylarsyl. Schlenk³ determined the molecular weight of the substance in boiling benzene but found no evidence of dissociation. According to Porter and Borgstrom,⁴ as well as Borgstrom and Dewar,⁵ molecular weight determinations in naphthalene by the cryo-

¹ Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913.

² References to the literature on hexa-arylethanes is to be found in "Organic Radicals," Gomberg, *Chemical Reviews*, **1**, 141 (1924); also in Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, 1924.

³ Schlenk, *Ann.*, **394**, 220 (1912).

⁴ Porter and Borgstrom, *J. Am. Chem. Soc.*, **41**, 2051 (1919).

⁵ Borgstrom and Dewar, *ibid.*, **44**, 2919 (1922).

scopic method indicate that tetraphenyldiarsyl is associated rather than dissociated.

It seemed to us that more favorable results might be obtained in the case of tetra-*p*-anisyl-, tetra- α -naphthyl- and tetrabiphenyldiarsyl; at least it has been found that the anisyl, naphthyl and biphenyl nuclei further dissociation in the hexa-arylethane group.⁶

We decided to investigate these tetra-aryldiarsyls and had intended to prepare them by reduction⁷ of the tetra-arylarsyl oxides, since satisfactory methods of preparation for these oxides have been developed.⁸ However, a much simpler procedure was found. The tetra-arylarsyl oxides are converted readily by the action of hydrogen chloride into the diarylarsyl chlorides and the latter react with sodium iodide to form the corresponding iodides. Interaction of the latter with metals, at ordinary temperature, yields the tetra-aryldiarsyls. For example, the halogen is removed quantitatively if diphenylarsyl iodide, dissolved in bromobenzene,⁹ is shaken vigorously with mercury for twenty minutes. Such a solution, in less than thirty seconds, absorbs almost exactly the quantity of oxygen¹⁰ calculated for the formation of a peroxide, $(C_6H_5)_2As-O-O-As(C_6H_5)_2$ and decolorizes instantly a carbon tetrachloride solution of iodine.

In fact, the solution obtained after removal of the halogen from diphenylarsyl iodide is strikingly similar in behavior toward oxygen and iodine to that obtained when triphenylmethyl chloride, dissolved in bromobenzene, is treated with mercury; however, in the former case the solution is colorless, in the latter it is yellow.

In order to obtain tetraphenyldiarsyl in the solid state, diphenylarsyl iodide was dissolved either in benzene or absolute ether and, after removal of the halogen by mercury, the solution was filtered and the solvent removed under diminished pressure. During these operations precaution must be taken to prevent oxygen from coming in contact with the material. The crystalline diarsyl, when dissolved in bromobenzene, absorbs the amount of oxygen calculated for peroxide formation.

The behavior of tetraphenyldiarsyl and other tetra-aryldiarsyls described in this paper indicates that these compounds dissociate to some

⁶ In the tetra-arylhydrazine series, according to Wieland, tetra-*p*-anisylhydrazine dissociates to a greater extent than tetraphenylhydrazine but tetrabiphenylhydrazine undergoes less dissociation than the phenyl analog.

⁷ Michaelis and Schulte, *Ber.*, **15**, 1952 (1882).

⁸ Blicke and Smith, *J. Am. Chem. Soc.*, **51**, 1558 (1929).

⁹ This solvent was chosen because of its comparatively low vapor pressure, an essential feature if the solution is to be used subsequently for an oxygen-absorption determination. As far as the removal of halogen and formation of the diarsyl is concerned, other solvents such as ether or benzene serve equally well.

¹⁰ The apparatus devised by Gomberg and Schoepfle, *J. Am. Chem. Soc.*, **39**, 1661 (1917), for oxygen absorption was employed.

extent into diarylarsyls, that is, divalent arsenic radicals. Molecular weight determinations of the various diarsyls are now being carried out in the hope that the dissociation, in some cases at least, is of such a magnitude that it can be detected by this method.

The behavior of other diarylarsyl iodides with mercury is described in the experimental part of this paper.

A further study of tetra-aryldiarsyls is in progress in this Laboratory and the action of metals on diarylstibinyl halides and on diarylbismuthyl halides is being investigated.

Experimental Part

Diphenylarsyl iodide, dissolved in bromobenzene, ether or benzene, reacts very rapidly at ordinary temperature with mercury, slower with molecular silver and zinc powder and very slowly, if at all, with magnesium powder or magnesium ribbon. In one instance $\frac{1}{200}$ mole of diphenylarsyl iodide, 6 g. of mercury and 15 cc. of bromobenzene were placed in the absorption bottle and the mixture was shaken continuously by hand. The amount of oxygen which had reacted after twenty minutes was 56 cc.; after thirty minutes, 59 cc. No further amount of oxygen was absorbed after an hour. The calculated quantity of oxygen required for peroxide formation is 56 cc.

A mixture prepared from 6 g. of mercury, 0.6 g. of iodine and 15 cc. of bromobenzene was rotated for four hours in a sealed tube. The mixture did not absorb oxygen; neither did diphenylarsyl iodide dissolved in bromobenzene absorb the gas.

It was found by analysis¹¹ of the mercury halide formed that mercury removes the halogen rapidly from di-*p*-tolyl-, di-*p*-anisyl-, di- α -naphthyl- and dibiphenylarsyl iodide.

Bromobenzene solutions obtained by shaking diphenyl-, di-*p*-tolyl- and di-*p*-anisyl iodide, respectively, with mercury, after complete removal of the iodine, absorb at once the calculated quantity of oxygen with the evolution of a considerable amount of heat. If the solution which has absorbed oxygen is allowed to remain in contact with the gas for a long period of time, a further *slow* absorption takes place due, probably, to the decomposition of the peroxide into secondary products which react with oxygen. A similar behavior is characteristic of triarylmethyl peroxides. In the case of solutions obtained from di- α -naphthyl- and dibiphenylarsyl iodide there was an immediate absorption of oxygen in excess of that required for the formation of a peroxide, the absorption varying from 125–130% of the calculated amount. At present we are unable to account for this phenomenon.

Relation between the Quantity of Oxygen Absorbed and the Amount of Halogen Removed.—Two sets of sealed tubes were rotated for definite periods of time. Each tube of the one set contained $\frac{1}{200}$ mole of diphenylarsyl iodide, 15 cc. of bromobenzene and 3.0 g. of molecular silver (80–100 mesh). Each tube of the second set contained one-fifth of the above quantities of material. At intervals one tube from each set was removed from the rotating apparatus. The tube which contained the larger quantities was used for oxygen absorption; the contents of the other tube were poured on a filter, the residue of silver and silver iodide was washed several times with boiling xylene and then with acetone. The mixture was removed from the filter and the silver dissolved with hot, dilute nitric acid. The silver iodide was filtered and weighed.

A comparison of Line 4 with Line 3 shows that the percentage of oxygen absorbed is comparable, within the limit of experimental error, to the

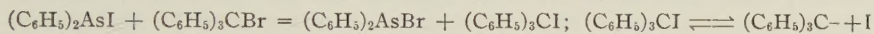
¹¹ The analytical procedure of Kohn, *Z. anorg. Chem.*, **59**, 108 (1908), was used but the iodine was determined volumetrically by the Volhard method.

percentage of silver iodide formed. The actual amount of oxygen absorbed, Line 2, is practically the same as that calculated, Line 5, from the quantity of silver iodide.

TABLE I
EXPERIMENTAL DATA

Time shaken, hours	6	11	24	48
O ₂ abs. after 1 min., cc., N.T.P.	14	26	41	53
Silver iodide, %	22	44	72	94
Oxygen absorbed, %	25	46	73	95
Abs. calcd. from AgI, cc.	12	25	40	52

It was found that diphenylarsyl iodide and triphenylmethyl bromide react instantly, when dissolved in bromobenzene, to form a deep red solution. The tendency for reaction is so great that when the two compounds are mixed in the solid state a red color develops at the points of contact. The solution absorbs oxygen rapidly. Undoubtedly the two compounds react in accordance with the following equation



However, the volume of oxygen absorbed (50 cc.) is greatly in excess of that calculated (28 cc.) for the amount of triphenylmethyl which could be produced. Other diarylarsyl iodides behave in an entirely analogous manner with triphenylmethyl bromide.

No color was developed when a mixture of diphenylarsyl bromide and triphenylmethyl bromide was dissolved in bromobenzene, and the solution did not absorb oxygen. No oxygen was absorbed by a mixture of diphenylarsyl bromide, iodine and bromobenzene.

A mixture of $1/200$ mole of diphenylarsyl iodide, 3 g. of silver and 15 cc. of bromobenzene was rotated for two days. The mixture absorbed 56 cc. of oxygen or 100% of the calculated amount. A similar mixture, except that $1/200$ mole of triphenylmethyl bromide was used in place of the arsyl iodide, absorbed under similar conditions 52 cc. of oxygen or 93% of the calculated amount. One four-hundredth mole of diphenylarsyl iodide, $1/400$ mole of triphenylmethyl bromide, 3 g. of silver and 15 cc. of bromobenzene were rotated for two days; the mixture absorbed 73 cc. of oxygen or 130% of the calculated amount.

Preparation and Properties of Tetraphenyldiarsyl.¹²—One-hundredth mole of diphenylarsyl iodide, 12 g. of mercury and 60 cc. of dry benzene¹³ were put into a bottle which had been filled previously with dry, oxygen-free nitrogen. The bottle was stoppered tightly and then shaken by fastening it to the rim of a slowly revolving wheel. After the halogen had been removed the mixture was filtered into an apparatus similar to that used for the isolation of triarylmethyls.¹⁴ The bulb of the apparatus was placed in a cone-shaped coil made from lead pipe, steam was passed through the latter

¹² This procedure applies also to the preparation of tetra-*p*-tolyl-diarsyl and tetra-*p*-anisyl-diarsyl.

¹³ The benzene had been saturated with dry, oxygen-free nitrogen and was preserved over sodium. Ether may be used in place of benzene as a solvent.

¹⁴ Gomberg and Cone, *Ber.*, **37**, 2033 (1904).

and most of the solvent in the bulb was removed under diminished pressure.¹⁵ The greater portion of the diarsyl separates as a colorless, crystalline precipitate. The contents of the bulb were treated with 20 cc. of dry, oxygen-free ether and the liquid poured out of the apparatus. The precipitate was dried by applying suction to the bulb and maintaining the latter at a temperature of 70–80° for three hours to insure complete removal of the solvent. The apparatus was then filled with nitrogen and the diarsyl transferred to a small test-tube in a stream of the gas.¹⁶ The compound melted at 120–125°.¹⁷

In several instances oxygen absorptions were made with the tetraphenyldiarsyl isolated from ether. It was found that 0.5440 g. of the diarsyl, dissolved in bromobenzene, absorbed after one minute 26 cc. (calculated amount, 26.5 cc.). In a second experiment 0.5005 g. of the material was dissolved in ethylene bromide. The solution absorbed 25 cc. (calculated amount, 24 cc.).

Potassium permanganate dissolved in acetone was added to tetraphenyldiarsyl dissolved in the same solvent. The diarsyl decolorized instantly the amount of permanganate required theoretically to convert the substance into diphenylarsinic acid, although the latter was not isolated. Tetraphenylarsyl oxide and diphenylarsyl iodide also decolorized immediately an acetone solution of potassium permanganate.

Tetraphenyldiarsyl, tetraphenylarsyl oxide and diphenylarsyl iodide all decolorized instantly iodine dissolved in carbon tetrachloride. In the case of the tetraphenyldiarsyl the exact amount of iodine was added which was necessary for the formation of the diphenylarsyl iodide. A black, gummy precipitate formed which was, no doubt, a periodide. The solution was decanted from the precipitate and after removal of the solvent the black, viscous residue was covered with water and treated with sulfur dioxide. A yellow, crystalline substance was obtained which, after recrystallization from alcohol, melted at 42–43°. This material was diphenylarsyl iodide.

That a solution of tetraphenyldiarsyl is stable toward light, at least in the presence of mercury salts, is shown by the following experiment: 1.78 g. ($1/200$ mole) of diphenylarsyl iodide, 6 g. of mercury and 15 cc. of bromobenzene were rotated for eighteen hours. The tube which contained the material was then placed outdoors for nineteen days. The contents of the tube absorbed the calculated amount of oxygen, that is, 56 cc.

Summary

It has been shown that a number of tetra-aryldiarsyls can be prepared readily, from the interaction of a diarylarsyl iodide and mercury.

Because of the extremely great reactivity of these compounds toward oxygen, and other reagents, it seems that their behavior can be explained best by the assumption that the tetra-aryldiarsyls dissociate spontaneously into diarylarsyls, that is, divalent arsenic radicals.

¹⁵ If all of the solvent was removed, the diarsyl obtained was somewhat gummy.

¹⁶ The diarsyls are so extremely reactive toward oxygen that it was found advisable to remove the compound from the apparatus in a large, specially designed box which was filled with dry carbon dioxide. All operations which involved exposure of the diarylarsyl, such as the preparation of pellets for molecular weight determinations, were carried out in this box.

¹⁷ Michaelis and Schulte, ref. 9, state that the compound melts at 135°; Borgstrom and Dewar, ref. 7, recorded the melting point as 130.5° (corr.).

